NIST Combinatorial Methods Center

FOCUSED PROJECTS
NON-PROPRIETARY RESEARCH AGREEMENT
APPENDIX A – INTERFACIAL TENSION MEASUREMENTS

Article 1. **INTRODUCTION**

High-throughput measurement tools for interfacial properties in emulsions will see immediate impact in a number of applications. Careful choice of a specific target area is critical to realizing a quick return for our members in the early stages of the project. The purpose of the focused project is to establish a commitment to active exchange between the participating members and to develop a valid test method for interfacial tension measurements of industrially relevant model systems. Our goal is to develop a method with deep context in industry, based on a strong foundation of fundamental science, and to make this project a model in itself of the range of perspective problems that can be addressed by using high-throughput microfluidics methods in polymer formulation technology.

By developing the use of μF instrumentation to measure the behavior of polymers in complex fluids, we aim to demonstrate new approaches to formulation science. With fast, flexible methods of designing and assembling milli-scale models of emulsion or colloid processing tools, high-throughput screening and optimization of new materials and discovery of new applications can be achieved across multiple stages of process development. Chemical suppliers and their customers will be able to obtain more and higher quality data relevant to the polymer additive properties critical to their business.

Most current μF technology is directed toward life science applications with devices designed primarily for low viscosity, aqueous solutions. We have developed a soft lithographic technique, which imparts solvent resistance to our devices and facilitates the integration of both aqueous and organic media. Using the existing suite of technology in the NIST Combinatorial Methods Center (NCMC), we can introduce high-throughput methods that span multiple compositions by varying the input of either phase. Combinatorial μF systems can then be developed to measure viscosity, interfacial tension, and stability of emulsions in an automated and high-throughput manner. Our systems will allow multiple feedstocks to be mixed in a range of compositions and their above-mentioned properties measured over a range of temperatures.

Article2. **BACKGROUND**

The interfacial tension in emulsions will be measured by monitoring drop deformation and retraction under a known flow field. The relaxation of a spheroidal droplet towards an equilibrium spherical shape is exponential under quiescent conditions: [1,2]

$$\alpha = \alpha_o \exp\{-t/\tau_d\},$$

where α is the droplet deformation = (L-B)/(L+B), defined by Taylor,[3] where L is the major axis of the spheroid and B is its minor axis. τ_d is the drop shape relaxation time $\tau_d = \eta_{eff}\, a_o/\alpha$, where a_o is the radius of the undistorted sphere, η_{eff} is a viscosity parameter $\eta_{eff} = \left[\frac{(2\hat{\eta}+3)(19\hat{\eta}+16)}{40(\hat{\eta}+1)}\right]\eta_c$,[2,3] and $\hat{\eta} = \eta_d/\eta_c$ is the relative viscosity of the drop compared to the matrix. A wide range of viscosity (with the viscosity of the more viscous component ranging from 0.1 Pa s to 1000 Pa s) and viscosity ratio (0 to 1000) can be studied. Having measured the viscosity of the components, the interfacial tension is measured from image analysis of the relaxation of drop shape. The drop size will be adjusted so that the shape relaxation time is in the range of 1/30 s to 1 s, so that rapid, high-throughput analysis is possible. In mixtures containing surfactant, equilibrium and dynamic properties of the surfactant can be investigated via Langmuir and Frumkin models.

References:

[1]A. Luciani, M. F. Champagne, and L. A. Utracki, “Interfacial tension coefficient from the retraction of ellipsoidal drops,” J. Polym. Sci. Polym. Phys. **35**, 1393 (1997).

[2]J. M. Rallison, “The deformation of small viscous drops and bubbles in shear flows,” Ann. Rev. Fluid Mech. **16**, 45-66 (1984).

[3]G. I. Taylor, “The viscosity of a fluid containing small drops of another fluid,” Proc. Roy. Soc. (London) **A138**, 41-48 (1932).

Article 3. **COLLABORATION AND DISSEMINATION**

A meeting will be held six weeks after the formal launch of the project as well as at six-month intervals for the duration of the project. Quarterly reports will be submitted to the members with updates more frequently via conference calls and other postings. In order to facilitate the collaboration, specifications for methods, instruments, programs, data analysis, and other aspects of this work will be available to members during the course of the project. A summary report will be provided within two months of the end of the project. The NCMC labs will be open to prearranged visits from member scientists interested in hands-on participation in method development.

As with base level membership in the NCMC, all of the research carried out in the Focused Project is non-proprietary and is intended for publication in the public domain. No proprietary information or materials will be solicited or accepted by NIST from member organizations. The scope of the work by NIST included in this focused project is limited as described in Article 5 below.

Article 4. **PROJECT DELIVERABLES**

4.1 **First year:**

4.1.1 Mixing methods for droplet phase materials (organics) will be developed that allow varying composition of polymeric surfactants and other additives.
4.1.2 Device geometries will be designed to produce droplets with controlled size of the organic phase in an aqueous medium with continuously varying properties.
4.1.3 Device geometries will be optimized using finite element analysis to produce flow fields for sheering and elongating droplets.
4.1.4 Instrumentation will be fabricated using a variety of methods including soft/traditional lithography, laser ablation or imprinting techniques as appropriate for model systems of interest to focused project members.

4.2 **Second year**

4.2.1 A high-throughput sample preparation method and a new milli-fluidic measurement platform will be integrated to demonstrate rapid characterization of polymer formulations.
4.2.2 Milli-fluidics measurements will be tested against industry standards and literature methods using model systems determined in cooperation with member organizations.
4.2.3 Application versatility will be demonstrated with validated measurements on several model systems of interest to member organizations.

Article 6. **FINANCIAL OBLIGATION**

Member’s project fees payable to NIST are set at $20,000 per year.